THE EISENHOWER LIBRARY
3 1151 02677 7098

67074

LIBRARY

OF THE

JOHNS HOPKINS UNIVERSITY.

Accepted
May 25/94

A Study of the Reaction of Certain Diazo Compounds with the Alcohols

Dissertation,
Submitted to the Johns Hopkins University
for the degree of Doctor of Philosophy
by
Frank Kenneth Cameron
1894.

H.N.M.

67074

The investigation described in this paper, was undertaken at the suggestion, and under the personal supervision, of Professor Ira Remsen, to whom, as also to Professor E. W. Morse, G. H. Williams, and Dr. J. S. Ames, I would here record my earnest acknowledgment of instruction, and encouragement, in my preparation for the doctorate.

Acknowledgement 2

Introduction 6

The Diazo-phenols. 8

Para-diazo-phenol Chloride with Ethyl Alcohol 9

Methyl Alcohol 9

Ethyl Alcohol and Sulphuric Acid 10

Ethyl Alcohol and Hydrochloric Acid 10

Ethyl Alcohol and Potassium Hydr- 10

[illegible] 11

[illegible] 11

Methyl Alcohol and Ammonia 11

Methyl Alcohol and Hydrochloric Acid 12

[illegible] 13

Ether and Sulphur Dioxide 13

Ether and Ammonia 14

[illegible] 15

Ortho-diazo-phenol Chloride 15

with Ethyl Alcohol 15

Methyl Alcohol 16

Ortho-diazo-phenol Chloride with Methyl Alcohol and Hydrochloric Acid 16

Methyl Alcohol and Sulphurous Dioxide 17

Meta-diazo-phenol Chloride 17

with Water 18

Water and Hydrochloric Acid 19

Ethyl Alcohol 19

[illegible] 1

Preparation of Chloro- and Bromo-diazo benzene Salts 20

[illegible] 21

Methyl Alcohol 22

Ortho-chlorodiazo-benzene Sulphate with Ethyl Alcohol 22

Methyl Alcohol 23

[illegible] 24

Meta-chloro-diazo-benzene Sulphate with Ethyl Alcohol 24

Methyl Alcohol 25

Para-chloro-diazo-benzene Nitrate with Ethyl Alcohol 26

Methyl Alcohol 27

Para-chloro-diazo-benzene Sulphate with Ethyl Alcohol 28

Para-chloro diazo-benzene Sulphate with Methyl Alcohol 29
Ortho-bromo-diazo-benzene Nitrate with Ethyl Alcohol 29
Methyl Alcohol 29
Ortho bromo-diazo benzene Sulphate with Ethyl Alcohol 30
[illegible] 30
[illegible] 31
Methyl Alcohol 31
Meta-bromo-diazo-benzene Sulphate with Ethyl Alcohol 32
Methyl Alcohol 32
Para-bromo-diazo-benzene Nitrate with Ethyl Alcohol 34
[illegible] 34
Para-bromo-diazo benzene Sulphate with Ethyl Alcohol 35
Methyl Alcohol 36
Summary 37
Conclusions 43
Autobiography 47
Notes 48

Introduction

Previous to the year 1870, it was supposed that the decompositions of diazo compounds with water or with alcohol were essentially different, a view first put forward by Griess, their discoverer. This view is more explicitly expressed by these equations:

$$C_6H_5 \cdot N_2 \cdot NO_3 + HOH = C_6H_5OH + N_2 + HNO_3 \quad \text{and}$$

$$C_6H_5 \cdot N_2 \cdot NO_3 + C_2H_5OH = C_6H_6 + N_2 + CH_3 \cdot CHO + HNO_3$$

But Wroblewski,[1] studying the decomposition of the isomeric [illegible] found that, at least, the reaction was analogous to the case where water was used, the grouping C_2H_5O entering in the place of $-O \cdot NO_2$. So that, taking the simplest example, the reaction would be,

$$C_6H_5 \cdot N_2 \cdot NO_3 + C_2H_5OH = C_6H_5 \cdot OC_2H_5 + N_2 + HNO_3$$

which has been found to be the case,[2] and is known, in general terms, as the alkoxy reaction, in contradistinction to that expressed by Griess' equation, and known as the hydroxy reaction.

In the light of the facts now known, it seems probable, that [illegible] the normal reaction [illegible]

[1] [illegible]

[illegible] the [illegible] the Barbieri-Acetabi work[1] the [illegible] of pressure or both, at which the decomposition takes place, the presence of certain oxygen, the action, and modification of certain substituting groups or elements in the benzene nucleus.

In this laboratory for some years past investigations on this subject have been carried on, under the personal direction of Professor Remsen, and the work is being continued at the present time.

The [illegible] investigations have recently been on the resistance of the hydroxyl group, and the elements [illegible] decomposition with ethyl and methyl alcohols.

The decomposition of ether compounds with water has been studied, it takes place normally, and it does not seem necessary in this connection to do more than refer to them for the sake of [illegible]

[1] Am. ch. Jour. 8:243. 9:387. 11:317. 15 105, 301, 320, 379. Dissertations 1893

[2] B. 4; 67-182. 777. B. 7; 905. B. 9; 1160. B 11. 1161. B 8; 502. Ann. 176; 30-45.

Ample quantities of ortho- and para-amidophenol hydrochlorates were on my bookshelf, and I was especially fortunate [illegible]

[illegible]

Para-diazophenol chloride was prepared by the method of Schmidt [illegible] para-amidophenol hydrochlorate was finely triturated in an agate mortar, and then poured into a beaker containing a saturated solution of nitrous oxide in alcohol and surrounded by a freezing mixture of crushed ice and hydrochloric acid. The mixture was stirred for about 5 min. then allowed to settle for a few minutes, and carefully decanted, so as to leave any undissolved amidosalt. The solution rapidly became dark blue. On the addition of much ether, and strongly cooling, the diazo compound separated in fine white crystals, which were filtered off with the aid of a pump, and dried on bibulous paper. It soon decomposed in the air, gradually becoming a bright crimson in color. Heated on platinum foil it decomposed with formation of violet fumes, much resembling in appearance iodine vapor, and left no residue when freshly [illegible]

20 gms. of the diazo compound, with 150 cc. ethyl alcohol, was placed in a flask, fitted with an inverted condenser, and slowly warmed. Decomposition commenced at about [illegible] when a gas began to be given off, and a strong odor of aldehyde perceived. The decomposition appeared completed in about an hour. The alcohol was then distilled off, the residue distilled with steam, and the distillates examined. As nearly as I was able to determine, the hydrogen [illegible] had taken place. [illegible] was present in considerable quantity, and was identified by precipitating with bromine water [illegible] melting point [illegible] of any other definite decomposition products. A considerable tarry residue remained after the distillation. This was examined, and attempts made to extract something definite with ether, benzene, hydrogen, chloroform, glacial acetic acid, acetone, etc, but without success.

20 gms. of the diazo compound was treated with 150 cc. methyl alcohol. Decomposition commenced on warming, but not so readily as in the last experiment, the [illegible] [illegible] [illegible]

[illegible]

completed in about 1½ hrs. After distilling with steam, the detailed [illegible] could be isolated.

Wreschny and Schuler,[1] studying the action of water on potassium [illegible] found that on heating the diazo-compound in the presence of picric acid. Therefore,

20 gms. of the diazo-compound was treated with ethyl alcohol containing 2% [illegible] decomposition took place much more rapidly and cleaner. Phenol and aldehyde were the only products that [illegible]

20 gms of the diazo compound was then decomposed in ethyl alcohol, saturated with hydrochloric acid, a stream of the dry gas being constantly passed through the solution during the reaction. The decomposition required about 5 hrs. for completion and was cleaner than in the last experiment. Phenol and aldehyde were the only products that could be identified.

20 gms. of the diazo compound was decomposed in ethyl alcohol containing 20% of [illegible] and the decomposition took

[1] Ber. 9: 1160.

place at once, and was very rapid, being completed in about 25 min.

A very large quantity of a tarry material was produced. Nothing

saturated with ammonia, and a stream of the gas, previously dried by passing over coarsely powdered quick-lime, was conducted through the solution during the reaction. The tube in which the decomposition took place was kept surrounded with ice water.

The decomposition commenced at once, and proceeded rapidly, being

could be detected. The odor of acetaldehyde was distinctly noticed,

20 grms. of the dioxy compound was decomposed with methyl alcohol

completion of the reaction, the alcohol was distilled off, and the residue distilled with steam. The presence of phenol in both distillates was proved. The water distillate on standing, changed color, to bright green, and finally an indistinct brownish ppt.

was obtained. To a bright red on the addition of an acid mixture of

[illegible] was added. The color changes were very sharp, and extremely delicate. An experiment made to determine the point, indicated that the color reaction was due to the regeneration of a dye stuff formed by the action of phenol on amido-phenol in alkaline solution. The presence of the amido-phenol was probably due to some of it dissolving in the alcohol, without being acted upon by the nitrous oxide, in the diazotizing process. This coloring matter was probably present in almost minute quantities, as it was when a [illegible]

20 gms. of the diazo compound was decomposed in Methyl alcohol saturated with hydrochloric acid, a stream of the dry gas being constantly passed through the reaction. The decomposition was slow and regular, 6 hours being necessary to boil for about 5 hrs. for completion. Phenol was the only product that could be identified.

There are several recorded cases of the decomposition of diazo compounds in the presence of sulphur dioxide. In this way Hübner[1] in certain cases was able to prepare the corresponding sulphinic acids. This suggested the following experiments:

40 gms. of the diazo compound was decomposed in methyl alcohol

[1] Ber. 10 1715

passed through the solution during the decomposition, which required about 8 hrs. at the boiling point of the alcohol for complete action.

The alcohol was distilled off and shown to contain phenol. The residue was then carefully dried over the water bath to insure elimination of any hydrochloric acid that might have remained as a product of the reaction. [illegible] It is therefore probable that a sulphonic acid was formed. No other definite product could be isolated.

It now seemed desirable to try the effect of sulphur dioxide in some neutral medium, which does not itself react with the diazo [illegible]

20 gms of the diazo compound was suspended in anhydrous ether, and a stream of sulphur dioxide passed in until the ether became saturated. Except a slight alteration in the color of the diazo compound, probably caused by the air brought in to contact with it in the early part of the experiment, there was no evidence of

2 gms. of the diazo compound was suspended in 20 grms of ether, the
tube surrounded with ice water, and a stream of dried ammonia
passed in. Decomposition commenced at once, and was quickly com-
pleted, the mass becoming black and tarry in appearance, but ap-
parently containing some granular material. The ether was filtered
off, and the residue dissolved in water. The aqueous solution
apparently contained some amido-phenol hydrochlorate, mixed with ammon-
ium chloride, but it was not possible to separate them, and no
definite statements can be made regarding the reaction.
Experiments were tried with the diazo compound and methyl alco-
hol, [illegible]
In all these cases, reaction took place at once, even under cooling, a
gas being given off. Water was then added sufficient to dissolve
out any unused sulphate. The gummy residue was then filtered
dried, and examined. No definite results however could be obtained.
The reaction is being studied in this laboratory at present in
[illegible]

Orthodiazo-phenol-chloride. After a number of experiments, I found that the best method on the whole, for the preparation of this compound, was to make a thin paste of ortho-diazo-phenol hydrochlorate in alcohol, keeping this well cooled by a freezing mixture, and to pass in rapidly a stream of nitrous oxide, previously well cooled, until the whole mass was in solution, and the gas was no longer absorbed. The dark colored solution resulting, was then poured into a large quantity of well cooled ether. The diazo salt soon separated out, but was generally slightly discolored greenish, which soon turned to brown, [illegible] Pure specimens were obtained by dissolving in methyl alcohol at the room temperature, and reprecipitating with strongly cooled ether. So soon became discolored on standing. [illegible] coal

20 gms. of the diazo compound was dissolved in ethyl alcohol, a marked diminution of temperature being noticed, and the solution becoming greenish in color. There was but little decomposition until the solution was warmed nearly to boiling, when it pro-

-cooled somewhat, and was completed in about 3 hrs. Alcohol was given off. The residue was distilled off, and on examination was shown to contain phenol. The residue was now transferred to a distilling bulb, and distilled, a mixture of alcohol and phenol distilling over until the thermometer indicated 178°-180° the boiling point of phenol. After standing at this point for some time, it rapidly [illegible] from the residue at the same time. This sublimate could not be identified, and appeared to be a mixture.

[illegible] ed lowering of the temperature. The decomposition was completed after [illegible] about 7 hrs. [illegible] Shown to contain phenol. The tarry residue was distilled, yielding phenol, but no other definite products.

50 gms. of the diazo compound was decomposed in methyl alcohol saturated [illegible] for boiling for about 9 hrs. The alcohol was distilled off, and shown to contain phenol. The residue was distilled with steam, more phenol passed over, and a very small quantity of a yellow crystalline solid

-ject in the condenser, which was shown by its melting point and physical properties, to be o-nitrophenol. Some of the original diazo salt was then distilled with steam, and was found to contain a small quantity of unreduced o-nitro-phenol.

40 gms. of the diazo compound was then decomposed with methyl alcohol, in the presence of sulphur dioxide. The decomposition was completed after boiling for about 9 hrs. Attempts to detect the presence of a sulphonic acid were unavailing. Phenol was the only definite substance that could be identified.

Meta-diazo-phenol chloride. The meta-amido-phenol hydrochloride was [illegible] described by [illegible] and the [illegible] was crystallized from concentrated solutions, by surrounding it with a freezing mixture. After a number of attempts to prepare the diazo [illegible] just sufficient 95% alcohol. A calculated amount of amyl nitrite was dissolved in about 5 c.c. the quantity of alcohol, and surrounded with a freezing mixture of crushed ice, and hydrochloric acid. Into this the solu-

[1] Am. Ch. Jour. 15, 39.

[illegible] of the [illegible] and [illegible] heavy, [illegible] very small [illegible] [illegible] time, [illegible] [illegible] [illegible]

which, after standing several days, deposited white needles, but much discolored by a black tarry residue, from which it was impossible to separate them by crystallization. The yield was very small.

30 gms. of the diazo compound was decomposed in water, containing about 10 % hydrochloric acid. The reaction appeared to be some- what slower than in the case of [illegible] until the distillate no longer gave a precipitate with bromine water. [illegible] was added and the [illegible] was observed, the precipitate [illegible] ethyl ether [illegible] it by a melting point [illegible].

15 gms. of the freshly prepared diazo compound was decomposed in ethyl alcohol. Decomposition commenced at once, and appeared complete in about an hour. It was then heated to boiling with apparently no further decomposition. The alcohol was [illegible] off, and steam to remove phenol. [illegible] with steam, more phenol came over, and a tarry residue was left in the flask. This residue was extracted with benzene, and chloroform, without success. It was then distilled, yielding a

small quantity of phenol, and then burning.

30 gms. of the diazo compound was decomposed with methyl alcohol. The decomposition commenced at once, and was completed in about an hour and a half. The alcohol was distilled off, and the residue was distilled with steam. Phenol was present in both distillates. No other product could be isolated.

Preparation of the chloro- and bromo-diazo-benzene salts.

The chlorodiazo-benzene salts, and the bromodiazo-benzene salts used in this investigation, were all prepared in the same manner, and one description will apply to them all, if the names of the particular anilines and acids be interpolated.

A weighed amount of the aniline was dissolved in a slight excess of the acid, and sufficient water added to make a thick paste when surrounded with a freezing mixture.

A rapid stream of nitrous oxide, prepared by decomposing strong nitric acid with arsenic trioxide, was passed through the paste, until the whole dissolved to a clear deep yellow

solution, and the gas was no longer absorbed. The diazo salt was then precipitated by adding to a strongly cooled mixture of [illegible] and ether. The precipitate was filtered off, washed with dry ether, and then dried on an unglazed plate and between papers.

[illegible] were effected in the usual manner. The [illegible] in the ice, and as cold as possible. Concentrated or suspicious specimens used.

The decompositions were carried on in suitable flasks [illegible] gauze, as this was found to be most convenient for [illegible] the froth. [illegible] a condenser.

Ortho-chlorodiazo-benzene

[illegible] of the diazo salt.

[illegible] It partially dissolved without decomposition. It was until decomposition had fairly commenced the lamp was withdrawn, and it [illegible]

-- alcohol in about an hour and a half. It was then boiled for a
half hour, to ensure complete decomposition. Nitrogen was
given off copiously during the reaction. Dis tilled with steam,
an oil passed over, which was separated, dried over calcium chloride
and weighed 7.6 gms. It was distilled, boiling at 132°, and was identified
as chlorobenzene. A small residue of tarry material was carefully
examined, but from it, nothing definite could be obtained.

.5 gms. of the diazo compound with 150 c.c. methyl alcohol, partially dissolved and decomposition commenced at once, and proceeded
slowly. After 24 hrs. it had ceased, but proceeded when the solution
was warmed, and appeared complete after boiling for an hour.

[illegible] steam in the usual way, and the oil weighed
7.5 gms. Boiled at 131°-133° and proved to be chlorobenzene, identical with that obtained in the last experiment. A small tarry
residue was examined, without obtaining any other definite product.

[illegible] yielded 24 gms. of the diazo salt.

[illegible] compound was [illegible]
salt decomposition [illegible]

Commenced, ish proceeded spontaneously, and developed so much heat, that the flask and its contents, had to be cooled, by dipping it from time to time, with a wet towel. The reaction was completed in about 3½ hrs and it was then heated to boiling for ½ hr. Aldehyde was given off during the reaction [illegible]

Separated, dried, weighed 9 gms, and distilled over at 132°. Showing the boiling [illegible] (not volatile).

25 gms. of the diazo compound with 200 c.c. methyl alcohol, gradually dissolved, decomposition beginning immediately, but proceeding very slowly. It was warmed from time to time, the decomposition being completed on the water bath. [illegible]

Dated, was dried, weighed 8.5 gms. and distilled at 132°, was identified as Chloro-benzene. No other products could be isolated.

Meta-Chloro-diazo-benzene

m-Chloro-diazo-benzene nitrate. 20 gms m-chloro-aniline, yielded 29 gms of the diazo salt.

20 gms [illegible] was treated with [illegible] alcohol. Warming from time to time, the decomposition was completed

in about 3½ hrs. Chloride was given off during the reaction. Dis-
[illegible] at 132°-134°, and was identified as chloro-benzene. No other def-
inite products could be isolated.

30 gms of the diazo compound with 300 cc. methyl alcohol, partial-
ly dissolved with some decomposition, which had proceeded but
little however, after standing for 6 hrs. It was then heated
boiling, and the decomposition was completed in an hour. On
cooling, a voluminous flocculent precipitate separated, which
was filtered off, dried, weighed 2-0.3 gms, was but slightly solu-
ble in alcohol or glacial acetic acid. The filtrate was distilled
with steam, an oil separating, which was dried, weighed 12 gms
and distilled over, for the most part at 187°-193°. A small residue
of tarry material was examined but yielded nothing definite.
[illegible]

110 gms. of the diazo salt, a practically theoretical yield.

30 gms. of the diazo compound with 300 c.c. of [illegible]
[illegible] and heated [illegible]
taneously, it being necessary to cool the flask by dipping it from

time to time with a wet towel. The decomposition was completed in about an hour, aldehyde being given off during the reaction. Distilled with steam an oil was separated, dried, weighed 15 gms. distilled over at 132° and was identified as chlorbenzene. No other defi-
nite product could be isolated.

30 gms. of the diazo compound with 300 c.c. methyl alcohol, partially dissolved and slowly decomposed. After standing 60 hrs. it was necessary to boil for about 2 hrs. to complete the decomposition. On cooling a flocculent precipitate, apparently identical with the one obtained in a former experiment, separated, was dried, and weighed 0.2 gms. The residue was distilled with steam, an oil was separated, dried, weighed 13. gms, and distilled for the most part at 187°–196°

110 gms. of the diazo compound, in two lots of 55 gms each, was
[illegible] 5 cc.
In the last experiment a flocculent precipitate separated after the
decomposition was complete [illegible] weighed
1.2 gms. The small quantity of this material and its behavior tow-
ards solvents, precluded a further study of it. The filtrate

was treated as in the last experiment, the greater portion of the oil distilling over at 187°–195°. No other definite products could be isolated. The three portions of oil, boiling above 186°, obtained [illegible] were now brought together and subjected to fractional distillation. After four distillations, was obtained a perfectly colorless, strongly refractive oil, possessing a peculiar aromatic odor, and but faintly suggestive of anisol. It boiled constantly at 198°. It was analyzed for chlorine, by the method of Carius

For meta chloro anisol,	Calculated	found
	24.88%	25.18% 25.12%

Para-chloro-diazo-benzene

p-Chlorodiazo-benzene nitrate. 30 gms. p-chloro-aniline yielded 36 gms of the diazo salt.

35 gms. of the diazo compound with 500 c.c. ethyl alcohol, partially [illegible] and [illegible] was completed in about 2 hrs. The alcohol was distilled off, and an oil precipitated from the distillate, by adding water. The product was distilled with steam, an oil coming over at 210°, estimated by some

high boiling material, which solidified in the condenser. The

to come over at 182°, but the thermometer showed [illegible]. The latter

The oil was probably chlorobenzene, containing a small quantity of p-chlorotoluene, but the quantity of material obtained was too small to make a good separation. The solid material was dissolved in caustic potash, filtered, evaporated to a concentrated solution, reprecipitated with hydrochloric acid, dried, and weighed 2 gms. After several recrystallizations from alcohol, it melted constantly at 87° and was identified as chloro-nitro-phenol of the formula $C_6H_3Cl(NO_2)(OH)$. No other definite products could be obtained.

25 gms of the azo compound with 300 c.c. methyl alcohol, partially dissolved without decomposition. On boiling for 2 hrs the decomposition was completed. The alcohol was distilled off, and an oil precipitated from it by adding water. The residue was distilled with steam, an oil coming over at first and then a solid material, as in the last experiment. The portion of oil was

brought together, dried, weighed 11 gms. and distilled, coming over at 200°, and identified as p-chloro-anisol. The solid material was dried, weighed 5.6 gms. It was dissolved in caustic potash, re crystallized, precipitated from a concentrated solution with dry hydrochloric acid, and recrystallized several times from alcohol, when it melted constantly at 87° and was identified as chloro-nitro-phenol $C_6H_3 \begin{matrix} Cl\ (1) \\ NO_2\ (3) \\ OH\ (4) \end{matrix}$ No other definite products could be isolated from the residue.

~~Para-chloro-benzo-diazo-benzene nitrate~~ 50 gms., ~~dissolved in 500 c.c.~~ 55 gms of the diazo salt a practically theoretical yield.

20 gms of the diazo compound with 200 c.c. ethyl alcohol, partially ~~dissolved and then decomposed~~ commenced, and then proceeded spontaneously, it being necessary to cool the flask, by wiping it from time to time with a wet towel. The decomposition was complete in about ~~an hour, and it was~~ boiled for a half hour longer. Distilled with steam, an oil was separated, dried, weighed 9 gms. and was redistilled, coming over at 131°. It was identified as chloro-benzene. Further examination of the residue yielded nothing definite. It was ~~not~~ fully examined for the presence

50 gms. of the diazo compound, with 350 c.c. methyl alcohol, heated

50 gms. of the diazo salt were decomposed with 300 c.c. methyl alcohol. The product was steam distilled, dried, weighed 15.4, and distilled at 200°. It was identified as p-chloro-anisol. No other product could be isolated from the residue.

Ortho-bromo-diazo-benzene

50 gms. of the diazo salt were decomposed with 300 c.c. methyl alcohol. The decomposition was carried out as usual, it being necessary to cool the flask from time to time. The decomposition was completed in 3½ hrs. It was then boiled 1½ hrs. Nitrogen was given off copiously. Distilled with steam, an oil was separated, dried, weighed 8 gms, distilled at 153°-154°, and was identified as bromo-benzene. No other definite product could be identified.

35 gms. of the diazo compound with 300 c.c. methyl alcohol,

Portion dissolved [illegible] decomposition. [illegible] boiling two hours
the decomposition was completed. The alcohol was distilled off, and
water, an oil precipitated by the addition of water. This distilled with
steam, the residue yielded more oil. The two portions were brought
together, dried, weighed 12 grms. and distilled over at 183°-186° and 270°
[illegible]
could be watched.

O-Bromobenzyl-benzoyl Sulphate. 25 grms. of bromobenzyl alcohol, 31 grms.
of the silver salt.

25 grms. of the silver compound with 250 cc. ether were placed in a flask with
the theoretical amount of benzoyl sulphate. The flask was closed
with a cork and allowed to stand for several hours, the contents
being shaken from time to time with a wet towel, to prevent too vigorous
[illegible]
half hour. It was then boiled for a quarter of an hour longer.
Distilled with steam, an oil was separated, dried, weighed 10 grms.
[illegible]
[illegible]
[illegible]
[illegible]

then sealed & boiling for 3 hrs. when the decomposition was completed.

[illegible] nation of the residue yielded nothing definite.

[illegible]

25 [illegible] dissolved with slight decomposition after standing about 20 hrs. Warmed until decomposition commenced, it proceeded spontaneously and was completed in about 3¼ hrs. It was then boiled for ½ hr. Hydride was given off during the reaction. Distilled with steam, an oil was separated, dried, weighed 11 gms, and distilled over at 153°-156°. It was redistilled and identified as bromo-benzene. No other definite [illegible] could be isolated.

30 gms. of the benzo compound with 200 c.c. methyl alcohol, partially dissolved with slight decomposition, after standing about 12 hrs. Sealed & boiling. The decomposition appeared completed in about an hour, and the boiling was continued for a half hour longer. On cooling

a voluminous flocculent precipitate separated, was filtered off dried and weighed 0.8 gm. The filtrate was distilled with steam, an oil separated, dried, which weighed 12 gms. In addition to this oil, the thermometer rose rapidly to 206°, and then slowly to 217°, by far the greater bulk coming over below 210°. The steam residue, yielded nothing definite.

[illegible] 3 gms. of the diazo salt.

25 gms. of the diazo compound with 250 c.c. ethyl alcohol, partially dissolved, with very slight decomposition, after standing about 20 hrs. [illegible] was completed in about an hour. It was then boiled for a half hour. Aldehyde was given off copiously, distilled with steam, an oil was separated, dried, and weighed 9 gms. It distilled entirely at 154° and was identified as bromobenzene. No other product could be found.

30 gms. of the diazo compound with 250 c.c. methyl alcohol, partially [illegible] 2 gms. water [illegible] boiling. The oil was [illegible] and dried [illegible]

boiling was continued for a half hour. On cooling a voluminous flocc[illegible]
[illegible] point, as in the last experiment. [illegible] cooling, the flocculent [illegible]
[illegible] were made to crystallize. [illegible]

The [illegible], distilled with steam, yielded 20.5 gms of oil, which for the most part distilled over at 206°-217°. This fraction was again distilled, yielding 15.5 gms of a colorless oil, strongly refracting, and with [illegible] was analyzed for bromine by the method of Carius.

Calculated for m-bromocumol	Found
$C_{10}H_{13}Br$ 47.39%	47.46% 47.83%

The oil was again rectified twice, and a fraction, about 8 gms. was obtained, which distilled constantly at 214°, and was analyzed.

1:2·7 % 1:3.5 % 1:3.6 %

ing some bromo-benzene in solution, which could not be completely separated, with the quantities at disposal. The residue was examined, but nothing definite obtained.

v.-Bromo-diazo-benzene nitrate. 10 gms. p-bromo-aniline yielded 12·6 gms. of the diazo salt

10 gms. of the diazo compound were dissolved in 200 c.c. methyl alcohol, and carefully heated on a water bath under a reflux condenser. The alcohol was distilled off, and some an oil separated on the addition of water. The residue was distilled with steam, an oil separating in the distillate. The two portions of oil were brought together, dried, and weighed 2·4 gms. It distilled at 154° and was identified as bromo-benzene. No other definite product could be obtained.

20 gms. of the diazo compound with 200 c.c. methyl alcohol, gradually dissolved without decomposition. On gently warming the decompo

[illegible] proceeds evenly, and was complete in about 1½ hrs. Shaken vig[orously] [illegible] 20 min. The alcohol was distilled off, and from it an oil precipitated by adding water. The residue was distilled with steam, no oil coming over at first, and then a yellow solid material. The portion [illegible] 220°-222° being identified as p-bromoanisol. The solid material was dissolved in caustic soda, recrystallized, and precipitated with hydrochloric acid. It weighed 1.5 gms. After crystallizing from alcohol, it melted sharply at 58° and was identified as bromonitrophenol of the formula $C_6H_3\begin{cases}Br\ (1)\\NO_2\ (3)\\OH\ (4)\end{cases}$ No other definite products could be isolated.

2-Bromodiazobenzene sulphate. 30 gms p-bromoaniline yielded 39 gms of the diazo salt.

20 gms of the diazo component with 200 c.c. ethyl alcohol, [illegible] was warmed until it dissolved, [illegible] reflux condenser, [illegible] 40 gms [illegible] [illegible] and it was then boiled for 20 min. Aldehyde was evolved copiously. Distilled with steam, an oil was separated, dried, weighed 9 gms, distilled

at 184°, and was identified as bromobenzene. No other product could be isolated.

35 gms. of the diazo compound with 300 c.c. methyl alcohol, [illegible] dissolved and brought to recombustion. After boiling 3 hrs the decomposition was complete. Distilled with steam, an oil was separated dried, and weighed 11.5 gms. It distilled at 220°-223°, and was identified as p-bromoanisol. No other definite product could be isolated.

The diazo-phenols

The experiments with the diazo-phenols here recorded are to be regarded as indecisive, as to the main object of this research. The only reactions that could be obtained may be represented by the following equations

$$C_6H_4\langle^{OH}_{N_2Cl} + HOH = C_6H_4\langle^{OH}_{OH} + N_2 + HCl.$$

$$C_6H_4\langle^{OH}_{N_2\cdot Cl} + CH_3\cdot OH = C_6H_5\cdot OH + N_2 + H.CHO + HCl.$$

$$C_6H_4\langle^{OH}_{N_2\cdot Cl} + C_2H_5\cdot OH = C_6H_5\cdot OH + N_2 + CH_3.CHO + HCl.$$

Or, in other words, the oxy reaction takes place, when a diazo ether not is decomposed with water, and the hydrogen reaction, with methyl or ethyl alcohol.

It does not seem probable, that the alkoxy reaction took place to any extent in any of the experiments recorded here, for the products that would have been formed, could have been readily recognized, from their crystalline form & behaviour.

But it became evident in the course of the work on these substances, that they were extremely unstable, very sensitive towards reagents, reacting themselves, with the products of decomposition, so that secondary reactions [illegible] mask the reactions expected from a priori considerations, if indeed

they took place at all. It is to be concluded that these substances are not suitable for this kind of investigation.

The chlorodiazo-benzenes

Ortho-chlorodiazobenzene salts with ethyl alcohol, as far as could be determined, gave the hydrogen reaction alone, as expressed by these equations:

$$C_6H_4\langle^{Cl\,(o)}_{N_2HSO_4} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4$$

Ortho-chlorodiazobenzene salts with methyl alcohol give the hydrogen reaction alone.

$$C_6H_4\langle^{Cl\,(o)}_{N_2NO_3} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + HNO_3$$

$$C_6H_4\langle^{Cl\,(o)}_{N_2HSO_4} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + H_2SO_4$$

Meta-chlorodiazobenzene salts with ethyl alcohol give the hydrogen reaction only.

$$C_6H_4\langle^{Cl\,(m)}_{N_2NO_3} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3$$

$$C_6H_4\langle^{Cl\,(m)}_{N_2HSO_4} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4$$

Meta-chlorodiazobenzene salts with methyl alcohol as were obtained. The substance is apparently predominantly giving meta-chloranisol as the principal product.

$$C_6H_4 \begin{cases} Cl\ (ortho) \\ N_2NO_3 \end{cases} + CH_3 \cdot OH = C_6H_4 \begin{cases} Cl\ (ortho) \\ OCH_3 \end{cases} + N_2 + HNO_3$$

$$C_6H_4 \begin{cases} Cl\ (ortho) \\ N_2HSO_4 \end{cases} + CH_3OH = C_6H_4 \begin{cases} Cl\ (ortho) \\ OCH_3 \end{cases} + N_2 + H_2SO_4$$

At the same time, it appeared that the hydrogen reaction took place to a small extent.

$$C_6H_4 \begin{cases} Cl\ (ortho) \\ N_2NO_3 \end{cases} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + HNO_3$$

$$C_6H_4 \begin{cases} Cl\ (ortho) \\ N_2HSO_4 \end{cases} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + H_2SO_4$$

There was also formed a small quantity of a well characterized solid whose nature was not determined.

Para-chlor-diazo-benzene nitrate and ethyl alcohol gave primarily the hydrogen reaction, as expressed thus:

$$C_6H_4 \begin{cases} Cl\ (p) \\ N_2NO_3 \end{cases} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3.$$

But at the same time, to no inconsiderable extent, the ethoxy reaction:

$$C_6H_4 \begin{cases} Cl\ (p) \\ N_2NO_3 \end{cases} + C_2H_5OH = C_6H_4 \begin{cases} OC_2H_5 \\ Cl \end{cases} + N_2 + HNO_3$$

accompanied with the formation of chlor-nitro-phenol $C_6H_3 \begin{cases} Cl\ (1) \\ NO_2\ (3) \\ OH\ (4) \end{cases}$.

The formation of a nitro-phenol seems to be strictly analogous to the cases already carefully studied by Remsen and Orndorff[1] of the action of diazo-benzene nitrate on ethyl alcohol and by Bronson[2] of the action of the diazo compound on methyl alcohol. From careful work on this bench, these investigators concluded that the nit

[1] Am. Chem. Jour. 7: 387.

[2] Ibid. [illegible] 1885, 98.

-Stanek was formed, by the elimination of nitrogen, and a molecular

-along during the past year, it has been suggested[1] that the nitroxy product is first formed, that this is then nitrated to some extent by the acid liberated in the reaction, and finally the nitro-ether thus formed, is saponified by boiling with the dilute acid, as in the formation of nitro-cresols, from the nitration of cresol ethers, studied by Staedel.[2] I regret that circumstances prevented me from studying the nitration of chloro-phenol ethers, in this connection.

Para-chloro-diazo-benzene sulphate and ethyl alcohol, as far as could be determined, gave only the hydrogen reaction

$$C_6H_4\langle^{Cl\,(p)}_{N_2.HSO_4} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4$$

These last two experiments suggest in a marked manner, what has been indicated[3] by other work, that the acid residue forming the salt of the diazo compound influences to some degree the nature of the reaction.

Para-

-oxy reaction entirely:

$$C_6H_4\langle^{Cl\,(p)}_{N_2NO_3} + CH_3OH = C_6H_5\langle^{Cl\,(p)}_{OCH_3} + N_2 + HNO_3$$

---

1) W. E. Chamberlin - Private Communication

2) [illegible]

3) Am. Ch. Jour. 11; 330.

At the same time was formed some chloro-nitro-toluene; $C_6H_3 < \overset{Cl\,(1)}{NO_2\,(3)}\overset{\quad}{CH_3\,(4)}$.

Para-chloro-diazo-benzene sulphate with methyl alcohol gave the methoxy reaction alone.

$$C_6H_4 < \overset{Cl\,(p)}{N_2HSO_4} + CH_3OH = C_6H_4 < \overset{Cl\,(p)}{OCH_3} + N_2 + H_2SO_4$$

Ortho-bromo-diazo-benzene.

Ortho-bromo-diazo-benzene salts with ethyl alcohol gave only the hydrogen reaction.

$$C_6H_4 < \overset{Br\,(o)}{N_2NO_3} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3$$

$$C_6H_4 < \overset{Br\,(o)}{N_2HSO_4} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4$$

Ortho-bromo-diazo-benzene salts with methyl alcohol gave only the hydrogen reaction.

$$C_6H_4 < \overset{Br\,(o)}{N_2NO_3} + CH_3OH = C_6H_5Br + N_2 + CH_2O + HNO_3$$

$$C_6H_4 < \overset{Br\,(o)}{N_2HSO_4} + CH_3OH = C_6H_5Br + N_2 + CH_2O + H_2SO_4$$

Meta-bromo-diazo-benzene salts with ethyl alcohol gave the hydrogen reaction.

$$C_6H_4 < \overset{Br\,(m)}{N_2NO_3} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3$$

$$C_6H_4 < \overset{Br\,(m)}{N_2HSO_4} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4$$

Meta-bromo-diazo-benzene salts with methyl alcohol gave principally the methoxy reaction.

$$C_6H_4 < \overset{Br\ (m)}{N_2 . NO_3} + CH_3OH = C_6H_4 < \overset{Br\ (m)}{O\,CH_3} + N_2 + HNO_3$$

$$C_6H_4 < \overset{Br\ (m)}{N_2 . HSO_4} + CH_3OH = C_6H_4 < \overset{Br\ (m)}{O\,CH_3} + N_2 + H_2SO_4$$

and at the same time to an undetermined, but probably small extent, the hydrogen reaction took place.

$$C_6H_4 < \overset{Br\ (m)}{N_2 . NO_3} + CH_3OH = C_6H_5Br + N_2 + CH_2O + HNO_3$$

$$C_6H_4 < \overset{Br\ (m)}{N_2 . HSO_4} + CH_3OH = C_6H_5Br + N_2 + CH_2O + H_2SO_4$$

Para-bromo-diazo-benzene salts with ethyl alcohol yielded only the hydrogen reaction.

$$C_6H_4 < \overset{Br\ (p)}{N_2 . NO_3} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3$$

$$C_6H_4 < \overset{Br\ (p)}{N_2 . HSO_4} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4$$

Para-bromo-diazo-benzene nitrate with methyl alcohol gave the methoxy reaction

$$C_6H_4 < \overset{Br\ (p)}{N_2 . NO_3} + CH_3OH = C_6H_4 < \overset{Br\ (p)}{O\,CH_3} + N_2 + HNO_3$$

and at the same time some bromo-nitro-benzene $C_6H_3 < \overset{Br\ (1)}{NO_2\ (3)}$ $\overset{}{OH\ (4)}$.

Para-bromo-diazo-benzene sulphate with methyl alcohol gave the methoxy reaction

$$C_6H_4 < \overset{Br\ (p)}{N_2 . HSO_4} + CH_3OH = C_6H_4 < \overset{Br\ (p)}{O\,CH_3} + N_2 + H_2SO_4.$$

Conclusions

There are now, excluding the diazo-phenols, five cases available for comparison and the discussion of the primary objects of this investigation, the decomposition with water, methyl and ethyl alcohol of diazo-benzene nitrate and the diazo-toluenes.

It has seemed to me better, on the whole, to discuss these cases together, and to facilitate this, I have tabulated the results of the experiments with methyl and with ethyl alcohol. There is no reason to believe that in any of these cases the reaction with water would be

With methyl alcohol

With ethyl alcohol

	Ortho	Meta	Para
Nitro-			
Amido-			
Chloro-			
Bromo-			
Iodo-			

A study of all the facts indicated by these tables, seems to me to warrant the following conclusions:-

1. The alkoxy reaction is normal, and the hydrogen reaction when it takes place, is a modification induced by special conditions.

2. Regarding water as the first member of the series, the more complex the alcohol, the greater the tendency towards the hydrogen reaction. This is in accordance with the view expressed by Metcalf.

3. That acid radicles, as COOH, Cl, Br, NO_2, etc, induce the hydrogen reaction, and their power in this respect, is probably in the order in which they are here named. This is in accordance with the

views expressed by Graham,[1] from a study of all the cases on record in which these radicles occur.

... [illegible] ...

While it would be unwarrantable to consider this last statement as proved, or as a finality, it seems to me a fair conclusion from a study of the above tables, and ~~in favor of~~ while awaiting further evidence, I feel justified in advancing it tentatively as a possible working hypothesis. It is to be observed, that it is not in accord with the view put forward by Orndorff, who regarded the para position as most favorable to the hydrogen reaching, and the meta, and ortho next in the order named. This view was advanced on the basis of a study of the diazo-toluenes when decomposed with [illegible] and I am not able to suggest any hypothesis by which they can be brought into accordance with the views here advanced. The further study of the decomposition of these diazo-toluenes with methyl alcohol is now in progress, but is not yet sufficiently advanced to aid in this

[1] Am. Ch. Jour. 5, 381.

The author of this dissertation, Frank Kenneth Cameron, was born in Baltimore, February 2nd, 1869. His preliminary education was received in part in the public schools, in part from private instruction. He entered this University in 1887 as a special student in mathematics and physics, matriculated in 1890, and received the baccalaureate degree in June 1891. Since then, he has been in this University devoting himself to the study of chemistry, under Remsen, Long and Venable, to whose instruction [illegible]